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(54) Non-conductive ink.

(57) A non-conductive ink-jet ink comprises a colourant, and, as a major component of the liquid phase, one or more polymerisable monomers in which the conductive component is soluble. The polymerisable monomers may comprise, by weight of the ink, up to 70% monofunctional monomer, up to 70% difunctional monomer, and 0 to 10% tri- or higher-functional monomer. The ink is suitable for piezoelectric drop-on-demand printing.

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Field of the Invention

This inventiòn relates to inks and their use in ink-jet printing.

Background of the Invention

The concept of piezoelectric ink-jet printing is based on the movement of a piezoelectric ceramic transducer when a voltage is applied to it. When the voltage is applied, the length of the ceramic decreases, creating a void which is filled with ink. When the voltage is removed, the ceramic expands to its full length and the excess ink is repelled, ejecting a drop of ink from the printhead. A fresh drop of ink is expelled on demand.

Inks for use in piezoelectric drop-on-demand ink-j t printing traditionally comprise a mixture of fatty acids, fatty esters and oil-soluble dyes. Such inks should be slow-drying, to prevent clogging of the nozzles; this constraint results in the process being suitable only for surfaces where the ink may dry through absorption. On non-absorbent surfaces, the ink remains wet for an undesirably long period of time.

US-A-4303924 discloses a radiation-curable ink-jet ink comprising, in addition to a colourant and a conductive component, 0 to 90% of monofunctional polymerisable monomer and 5 to 80% of multifunctional polymerisable monomer. Th colourant is a dye. The conductive component is oil-soluble. It is indicated that there may be 0% organic solvent, but all the given Examples contain more than 10% of such a solvent which, together with the high content of trifunctional monomer, provides a liquid phase in which the conductive component is soluble. If solvent were absent, there would be no medium for dissolution of the conductive component, and it is unlikely that the viscosity of the ink would be sufficiently low for ink-jet printing. Nevertheless, the presence of organic solvent presents the problem that the ink may dry in an open nozzle. The ink must apparently be used in an inert gas atmosphere, which is a considerable disadvantage.

EP-A-0407054 discloses an ultra-violet jet ink comprising a curable adhesive thinned with solvents which, at least in the Examples, invariably includ at least the organic solvent methyl ethyl ketone. This composition also presents the problem that the ink may dry in the nozzle.

EP-A-0465039 describes an ink-jet ink which meets the given constraints but which avoids the use of volatile, flammable, environmentally-undesirable solvents, and can be used in air. That ink comprises a colourant, a polar conductive component and, as the or a major component of at least the liquid phase, one or more polymerisable monomers in which the conductive component is soluble.

Summary of the Invention

An ink according to the present invention is non-conductive, and is suitable for use in piezoelectric drop-on-demand systems. By comparison with the ink described in EP-A-0465039, no conductive component is required, and the viscosity may be somewhat higher, e.g. up to 40 or 50 cP at 25°C; therefore, the novel composition may comprise a higher colourant content, providing enhanced contrast, and also an additional component that is a polymeric or other material having a thickening or other function, e.g. providing enhanced adhesion to a printed substrate.

An ink of the invention has a number of other desirable characteristics and advantages, which are summarised below. Perhaps most importantly, inks of the invention are suitable for all types of ink-jet printing, especially bubble jet or other drop-on-demand printing, and also flexographic and lithographic printing, based on non-volatile monomer molecules. Such monomer molecules are thermally-stable, non-flammable, low viscosity liquids and exhibit low odour and low toxicity. These liquids are designed to replace all traditional volatile solvents and binders used in known ink-jet formulations. The ink may also be designed with these or a range of solvents and binders.

Description of the Invention

An ink-jet formulation of the invention will usually comprise mixtures of monomers possessing different degrees of functionality, including combinations of mono, di, tri and higher functionality material. Such materials are capable of being cured by the application of UV irradiation, for which purpose the formulation may contain a photoinitiator and/or a photoactivator. Further, in addition to a colourant, the formulation may comprise conventional ingredients such as stabilisers, surfactants and wetting agents.

Upon printing, the droplet of ink is delivered to the substrate surface and converted to a dry film or dot by cross-linking or polymerising the monomer molecules by the action of an external energy source, adjacent to the printer, focused on the printing area. As an example, the external energy source may be a UV light source. The UV light source initiates the polymerisation process, which typically takes less than 0.5 sec. The preferred light source emits UV-A light only, e.g. at a wavelength of 315-400 nm, eliminating the need for extraction due to the production of ozone found with UV-B or UV-C light sources.

The choice of materials is wide and will depend on the application and properties required. As a means to highlight the principle, an ink-jet formulation may be designed to provide high solvent resistance by incorporating a relatively large proportion of higher functional monomer, thus producing, once cured, a highly cross-linked insoluble film.

A range of commercial monomers, e.g. having acrylic, vinyl or epoxy functional groups, photoinitiators and photoactivators is available and suitable for use in an ink-jet formulation, capable of polymerisation by UV light. The reaction may proceed through addition polymerisation; all reactants are converted to the final polymeric binder, leaving no by-product or trace of liquid. This reaction can proceed in two ways, either by a free-radical mechanism or by the formation of a cationic species.

Suitable monofunctional monomers that cure by a free-radical mechanism include vinyl compounds and (meth)acrylic acid esters. Specific examples are octyl acrylate, decyl acrylate, nonylphenol ethoxylate acrylate, N-vinylpyrollidone, ethyl diglycol acrylate, isobornyl acrylate, ethylhexyl acrylate, lauryl acrylate, butanediol monoacrylate, β-carboxyethyl acrylate, isobutyl acrylate, polypropylene glycol monomethacrylate and 2-hydroxyethyl methacrylate.

Suitable monofunctional monomers that cure by a cationic mechanism include vinyl ethers, monofunctional cycloaliphatic epoxides and α-epoxides. A specific example is isodecyl glycidyl ether.

It is preferred that some monofunctional monomer is present in the novel ink, since such materials have low viscosity. However, such materials will not usually be the sole polymerisable component, since some cross-linking is desirable, in order that polymerisation leads rapidly to a dry ink. The amount of monofunctional monomer in the formulation may be up to 70%, e.g. 25 to 60%, by weight.

In order to provide a balance of properties, the novel ink will almost invariably include some difunctional material, e.g. in an amount of up to 70%, preferably 20 to 60%, more preferably 30 to 50%, by weight of the formulation. Lower difunctional monomer contents are associated with longer ink drying times.

Suitable difunctional monomers that cure by a free-radical mechanism include difunctional (meth)acrylic acid esters, e.g. hexanediol di-(meth)acrylate, tetraethylene glycol diacrylate, tripropylene glycol diacrylate, butanediol diacrylate, polyethylene glycol diacrylates and triethylene glycol dimethacrylate. Suitable difunctional monomers that cure by a cationic mechanism include triethylene glycol divinyl ether, 1,4-cyclohexanedimethanol divinyl ether, butanediol diglycidyl eth r and difunctional cycloaliphatic epoxide resins.

Trifunctional monomers which may used in the invention include ethoxylated trimethylolpropane triacrylate. If present (for the reasons given above), tri- or higher functional components will usually comprise up to 10% by weight of the formulation.

The lower functional monomers comprise at least the major component of the liquid phase. The total content of polymerisable monomers in the ink will usually be 50 to 95%, e.g. at least 70% and often at least 80%, by weight of the formulation.

Suitable photoinitiators, especially for free-radical curing, include 2-hydroxy-2-methyl-1-phenylpropan-1-one, acrylic ketones, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinylpropanone, 2,2-dimethoxy-1,2-diphenylethan-1-one, benzophenone, isopropylthioxanthone and p-phenylbenzophenone. A photoinitiator suitable for the cationic curing mechanism is a triarylsulphonium hexafluoroantimonate salt.

Suitable photoactivators and photosynergists include ethyl 4-(dimethylamino)benzoate, N-methyldiethanolamine and 2-ethylhexyl dimethylaminobenzoate. Such materials will generally be required only for free-radical curing.

The choice of colourant for a monomer-based ink-jet ink is important, but it is possible to produce either a dye-based monomer ink or a disperse pigmented monomer-based ink of the invention. The use of pigment can provide faster curing, reflecting faster printing and enhanced solvent resistance.

A range of colours can be achieved, including black. The problem with black UV curable inks is the strong absorbence of light preventing successful curing or polymerisation. A black ink of the invention may comprise a mixture of dyes of different colours, which allows UV light at a discrete wavelength to penetrate and to initiate polymerisation, to produce a black-coloured film.

Suitable colourants include carbon black pigment, titanium dioxide pigment, ink-jet dyes including metal azo complex dyestuffs and mixtures of coloured dyestuffs. The colourant may be present in dispersion, if necessary in the form of particles coated with a material, e.g. a polymer, that is compatible with the liquid phase components.

Further, in addition to a colourant, the formulation may comprise conventional ingredients such as stabilisers, surfactants, wetting agents, polymers and viscosity modifiers.

The additional component may be a polym r incorporated in order to increase the viscosity of

the monomer blend, but may also be used to improve the adhesion and mechanical properties of the printed droplet. The range of suitable polymers is vast; suitable polymers include polyvinyl butyral, nitrocellulose, polyketones, polyamides, polyesters, and acrylic materials. The amount of this component in the formulation is, for example, 1 to 25%, e.g. about 5% by weight.

Alternatively, an ink-jet formulation of the invention may comprise a combination of low molecular weight multi-functional ethylenically-unsaturated or epoxy functional prepolymers with low viscosity monomers of various functionalities. Such materials are capable of being cross-linked by the application of ultraviolet light, for which purpose the formulation may contain a photoinitiator and/or a photoactivator.

A wide range of commercial prepolymers, e.g. having acrylic, vinyl, thiol or epoxy functional groups, photoinitiators and photoactivators is available. Such materials are suitable for use in an ink-jet formulation, capable of polymerisation by UV light. The reaction may proceed through addition polymerisation; all the reactants are converted to th final polymeric binder, leaving no byproducts or trace of liquid. This reaction can proceed in two ways, either by a free-radical mechanism or by th formation of an ionic species.

Suitable prepolymers which may react through th free-radical polymerisation include epoxy acrylates, polyester acrylates and polyurethane acrylates. Suitable prepolymers which may cross-link through a cationic mechanism include cycloaliphatic epoxides, and multifunctional vinyl ethers.

Cationic-polymerisable formulations of the type described above may also include hydroxyl-containing materials that copolymerise with the epoxide materials by acting as chain-transfer agents, improving the formulation cure speed. These materials may also be used to improve the flexibility of the final cured material.

It is also possible to combine the use of cationic and free-radical reactive materials in the sam formulation. Such a hybrid system can show improved cure speed over purely cationic systems. The hybrid system also possesses better mechanical properties, e.g. with respect to adhesion and abrasion resistance, in the cured state than the free radical systems alone.

By way of illustration of the present invention, either Example given in EP-A-0465039 is modified by substituting th KSCN by 5% polyvinyl butyral.

Claims

1. A non-conductive ink comprising a colourant and, as a major component of the liquid phase, one or more polymerisable monomers.

2. An ink according to claim 1, which comprises 50 to 95% by weight of polymerisable monomers.

3. An ink according to claim 1 or claim 2, which comprises, by weight thereof, up to 70% monofunctional monomer, up to 70% difunctional monomer, and 0 to 10% tri- or higher-functional monomer.

4. An ink according to claim 3, which comprises 25 to 60% by weight monofunctional monomer and 20 to 60% by weight difunctional monomer.

5. An ink according to any preceding claim, which is UV-A light-curable.

6. An ink according to any preceding claim, which comprises a photoinitiator and, optionally, a photoactivator.

7. An ink according to claim 6, which comprises 1 to 10% by weight photoinitiator and 0 to 5% by weight photoactivator.

8. An ink according to any preceding claim, which additionally comprises a polymeric or further polymerisable component adapted to provide increased viscosity.

9. An ink according to claim 8, which comprises a cationic-curable polymerisable component.

10. An ink according to any preceding claim, which comprises 0.5 to 5% by weight of colourant.

11. An ink according to any preceding claim wherein the colourant is black.

12. An ink according to any preceding claim, wherein the colourant is a dispersed pigment.

13. An ink according to any preceding claim, which contains no more than a minor proportion of non-polymerisabl volatile organic solvent.

14. An ink according to claim 13, which contains no volatile organic solvent.

15. A method of printing a substrate by piezo-electric drop-on-demand ink-jet printing, in which the ink-jet ink is as defined in any preceding claim.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 9263

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	US-A-4 303 924 (AINSLIE T. YOUNG) * claims * * example 2 * ---	1-15	C09D11/00
A	GB-A-2 004 904 (M & T CHEMICALS) -----	1-8	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 FEBRUARY 1993	CATURLA VICENTE V.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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